

Supplementary material

Title:

Methane (CH₄) sources in Krakow, Poland: insights from isotope analysis

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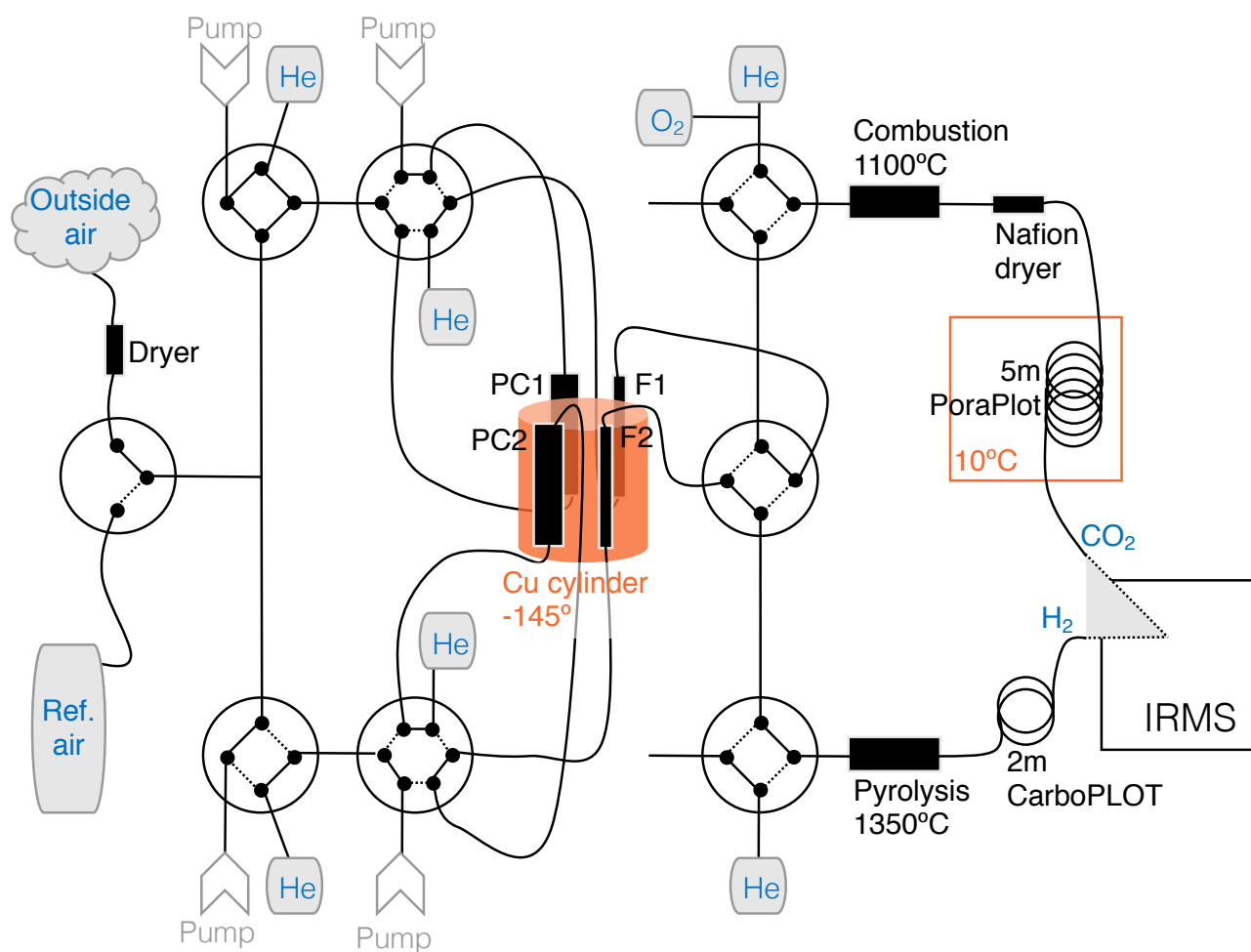


Figure S1: Diagram of the extraction system for methane isotopic measurements in ambient air. PC: pre-concentration, F: focus traps, two 10 cm stainless steel tubes (1/8" and 1/16" o.d., respectively) filled with 2 cm HayeSep D in the centre and glass beads at both ends.

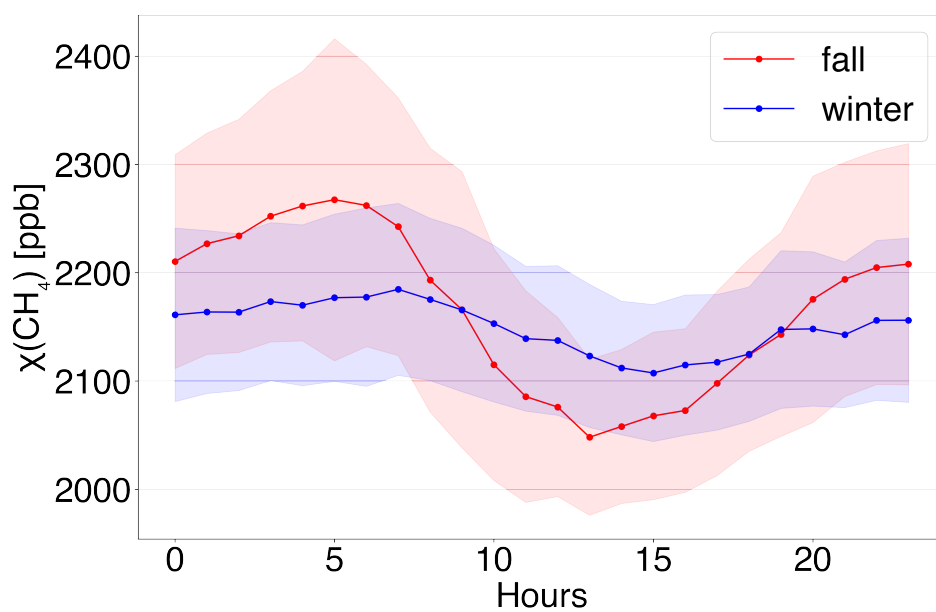


Figure S2: CH_4 mole fraction hourly averages during the fall (September 14 to November 15, 2018). Size of shaded area is 1σ .

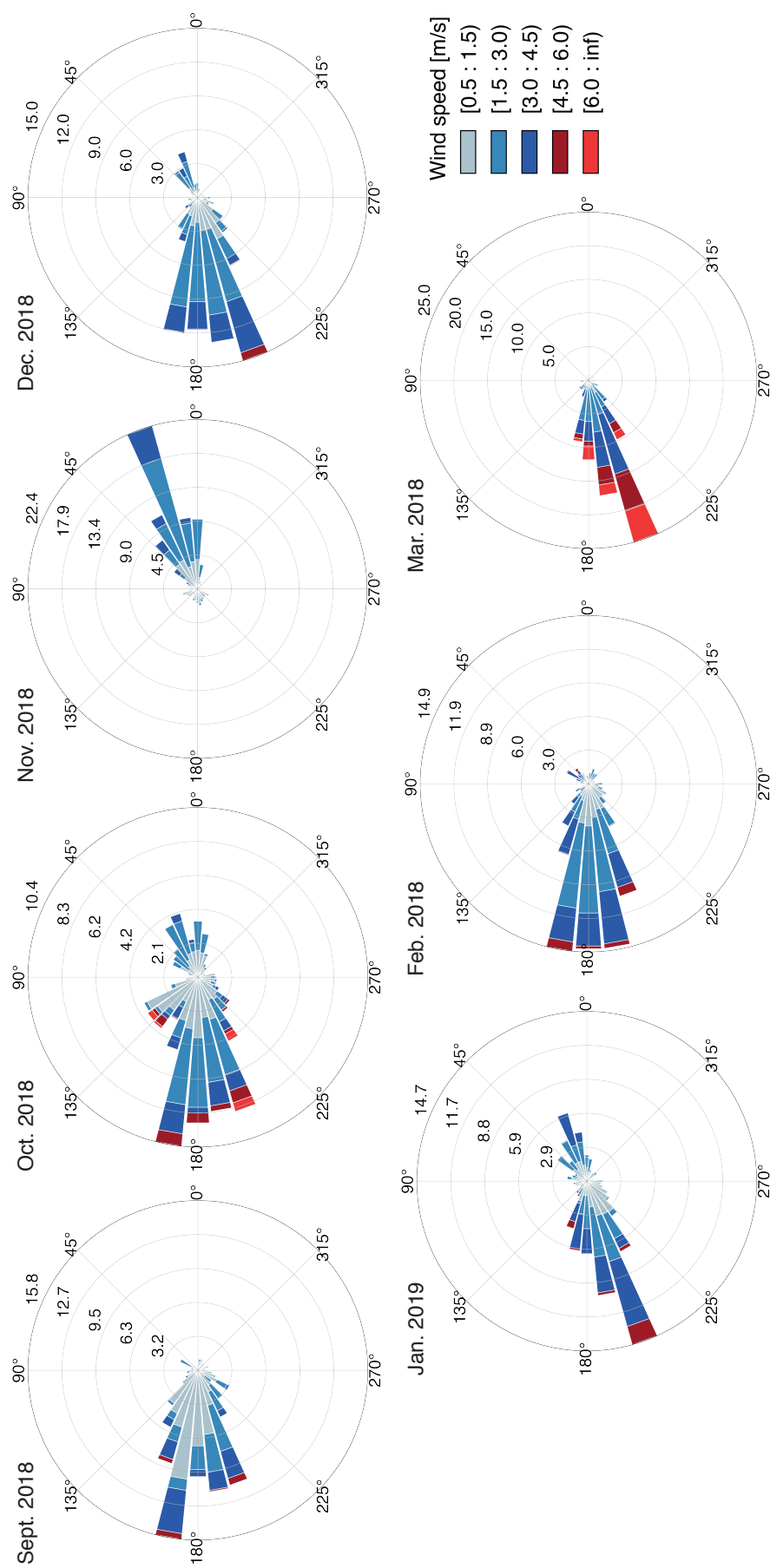


Figure S3: Monthly wind directions during the ambient air measurement period at the measurement location. Bar lengths are percentages of records from that wind direction during the specified month; colours define the wind speed range (legend).

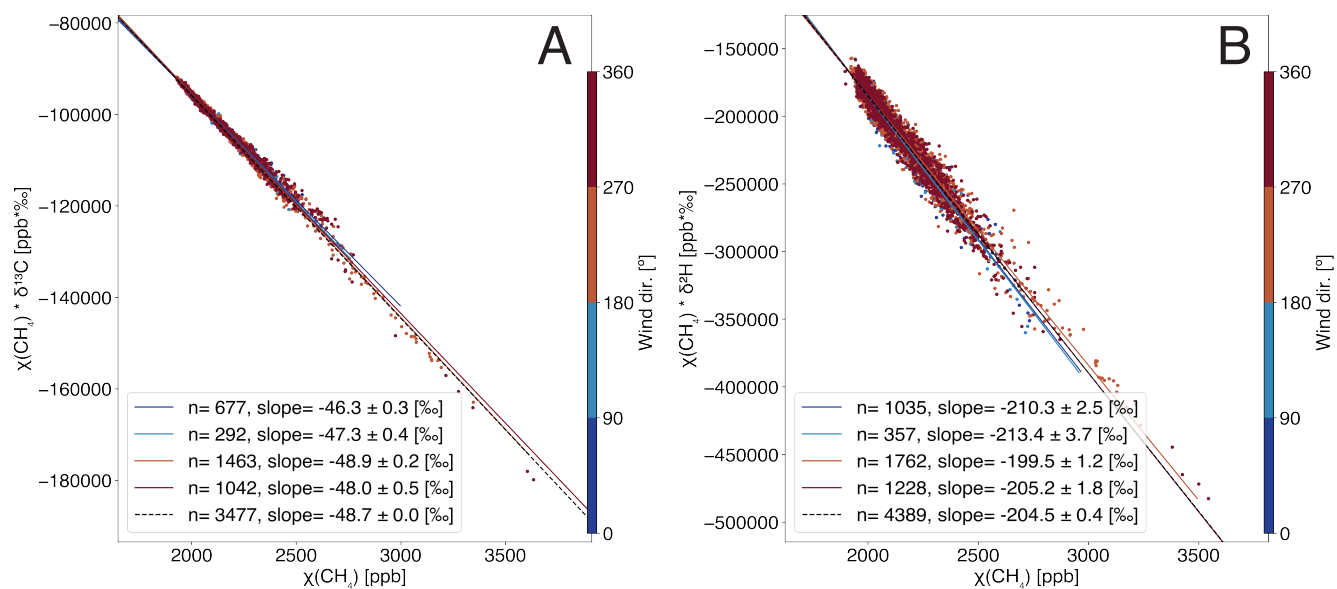


Figure S4: Miller-Tans plots using all the **A.** $\delta^{13}\text{C}\text{-CH}_4$ and **B.** $\delta^2\text{H}\text{-CH}_4$ data in ambient air collected during the measurement period. The regressions were made with all data points (black dotted line), or only associated with north-east winds (dark blue), south-east winds (light blue), south-west winds (light red) and north-west winds (dark red), using the bivariate correlated errors and intrinsic scatter (BCES) method (Akritas and Bershadsky 1996)

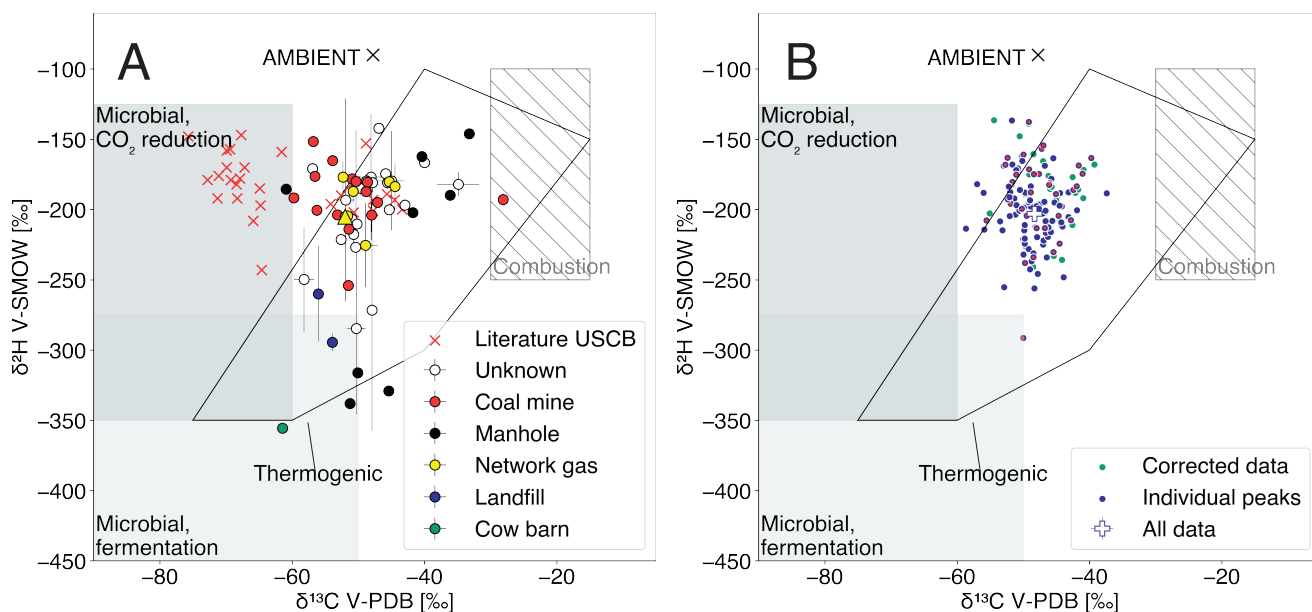


Figure S5: Dual isotope diagrams with signature ranges of specific CH_4 formation processes, reproduced from Milkov and Etiope (2018). **A.** Source signatures of the sampled sites around Krakow (coloured circles) and in the USCBA (red crosses; Kotarba 2001, Kotarba and Pluta 2009 and Kedzior et al. 2013). **B.** Source signatures of the peaks measured in the ambient air time series. Points marked with red center correspond to the period where observed a mismatch in the mole fractions between the IRMS and CRDS instruments. Green points: source signatures obtained when correcting the IRMS mole fractions to the CRDS ones. The peak source signatures were not significantly affected and therefore we used the original data.

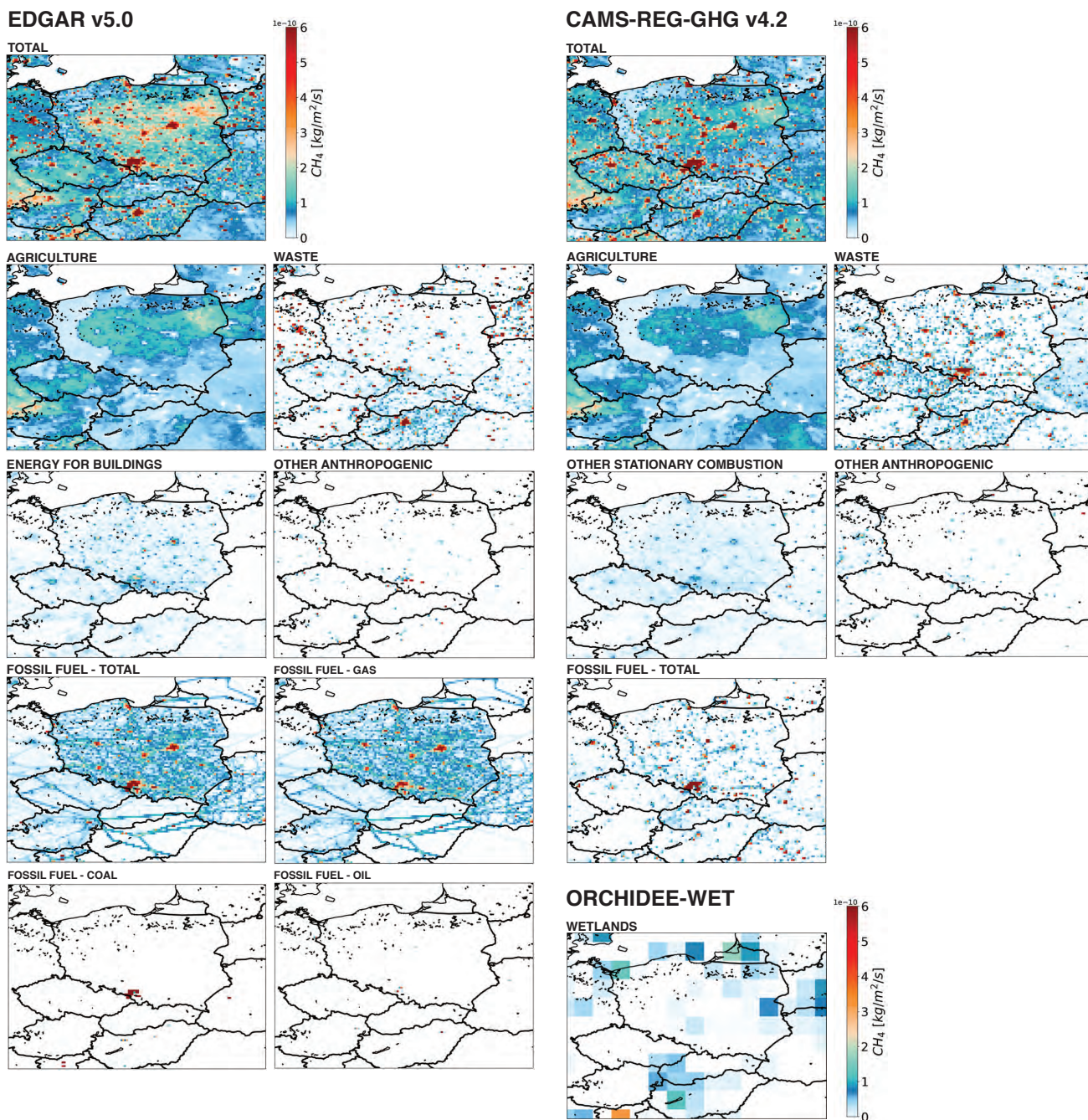


Figure S6: CH_4 emission rates over the domain used in CHIMERE, from two inventories: EDGAR v5.0 (left columns) and CAMS-REG v4.2 (right column). Emissions from the waste category are much higher in CAMS compared to EDGAR, for discussion see main text.

Table S1: Keeling plot results at all the sampled locations in the Krakow urban area and the USCB. Reported isotopic source signatures are the Keeling plot y-intercepts with reported uncertainties as $\pm 1\sigma$. Linear regressions were made using a weighted orthogonal distance regression method described in Boggs et al. (1992). In the case of $\delta^{13}\text{C}$, the r^2 indicates sometimes a poor correlation. This happens when the sampled source and background $\delta^{13}\text{C}$ values very close so that the slope of the fit line is close to 0.

Sampled location	Source	Date	$\chi(\text{CH}_4)$ [ppb]	excess	$\delta^{13}\text{C}$ VPDB [‰]	$\delta^2\text{H}$ VSMOW [‰]	n sam- ples	r^2 ($\delta^{13}\text{C}$)	r^2 ($\delta^2\text{H}$)
Barycz landfill	Landfill	24/05/2018	241		-56.0 $\pm$ 0.6	-260 $\pm$ 34	4	0.91	0.70
Borynia III	Coal mine	27/05/2018	6342		-56.3 $\pm$ 0.1	-201 $\pm$ 4	3	1.00	0.97
Zofiofka	Coal mine	27/05/2018	7049		-56.6 $\pm$ 0.0	-176 $\pm$ 1	4	1.00	0.75
Pniówek IV	Coal mine	27/05/2018	16885		-48.6 $\pm$ 0.1	-181 $\pm$ 1	6	0.79	0.96
Pniówek V	Coal mine	27/05/2018	85906		-47.1 $\pm$ 0.0	-195 $\pm$ 1	6	0.63	0.94
Pustelnik	Unknown	28/05/2018	657		-56.9 $\pm$ 0.3	-171 $\pm$ 4	8	0.75	0.74
Krupinski III	Coal mine	28/05/2018	4496		-56.8 $\pm$ 0.0	-152 $\pm$ 0	3	0.99	0.98
Pniówek III	Coal mine	28/05/2018	10118		-53.9 $\pm$ 0.1	-165 $\pm$ 1	5	0.96	0.78
Borynia VI	Coal mine	28/05/2018	20098		-51.0 $\pm$ 0.0	-178 $\pm$ 1	3	0.74	0.87
Pniówek III-b	Coal mine	28/05/2018	1997982		-53.2 $\pm$ 0.4	-204 $\pm$ 1	2	1.00	1.00
Pniówek IV-b	Coal mine	28/05/2018	1997982		-48.8 $\pm$ 0.1	-187 $\pm$ 4	2	1.00	1.00
Pniówek V-b	Coal mine	28/05/2018	1997982		-51.5 $\pm$ 0.1	-254 $\pm$ 1	2	1.00	1.00
Brzeszcze IV	Unknown	29/05/2018	6670		-46.9 $\pm$ 0.0	-142 $\pm$ 1	4	0.88	0.98
Silesia	Coal mine	29/05/2018	11666		-59.8 $\pm$ 0.0	-192 $\pm$ 3	4	0.80	0.97
ArcelorMittal, Mrozowa	Unknown	05/02/2019	133		-48.1 $\pm$ 2.3	-177 $\pm$ 45	4	-0.96	0.82
Instytut Zootechniki, Balice	Unknown	05/02/2019	142		-45.0 $\pm$ 2.0	-180 $\pm$ 35	4	-0.82	0.92
Pipeline, Senatorska	Network gas	05/02/2019	188		-48.9 $\pm$ 1.9	-225 $\pm$ 30	4	0.15	0.83
Pipeline, Balice	Network gas	05/02/2019	806		-50.8 $\pm$ 0.6	-187 $\pm$ 8	4	0.91	0.99
Ujastek Mogilski	Unknown	05/02/2019	1232		-43.0 $\pm$ 0.2	-197 $\pm$ 4	4	0.97	1.00
Sewage cover, Grunwaldski bridge	Manhole	05/02/2019	2787		-50.1 $\pm$ 0.1	-316 $\pm$ 2	4	1.00	1.00
Sewage cover, Kujawy STP	Manhole	05/02/2019	205536		-45.4 $\pm$ 0.1	-329 $\pm$ 3	4	0.94	1.00
Fishery ponds, Mydlniki	Unknown	06/02/2019	373		-34.9 $\pm$ 3.2	-182 $\pm$ 9	4	0.95	1.00
Liszki	Unknown	06/02/2019	189		-51.9 $\pm$ 1.4	-193 $\pm$ 72	4	0.78	0.79
Minikow	Unknown	06/02/2019	183		-50.3 $\pm$ 1.4	-285 $\pm$ 61	3	0.60	0.92
Polska Spółka Gazownictwa compressor station, Balicka	Network gas	06/02/2019	729		-44.4 $\pm$ 0.7	-184 $\pm$ 17	4	0.95	0.99
Vlastimila Hofmana	Unknown	06/02/2019	1332		-45.6 $\pm$ 0.1	-181 $\pm$ 5	5	0.23	0.96
Gas valve, Balicka	Network gas	06/02/2019	7461		-45.3 $\pm$ 0.1	-180 $\pm$ 2	4	1.00	0.99
Lewiatan, Kryspinów	Unknown	06/02/2019	15748		-45.9 $\pm$ 0.1	-175 $\pm$ 1	4	0.99	1.00
AGH, white tank	Unknown	07/02/2019	993		-40.0 $\pm$ 0.4	-167 $\pm$ 4	4	0.90	0.89
AGH, sewage cover W	Manhole	07/02/2019	1714		-60.9 $\pm$ 0.8	-186 $\pm$ 4	2	1.00	1.00
AGH, sewage cover SW	Manhole	07/02/2019	7058		-41.8 $\pm$ 0.0	-202 $\pm$ 2	3	1.00	1.00
Vlastimila Hofmana -bis	Unknown	19/03/2019	545		-50.7 $\pm$ 0.3	-218 $\pm$ 6	4	0.34	0.99
Grota-Roweckiego x Kobierzynska	Unknown	19/03/2019	578		-49.7 $\pm$ 0.4	-185 $\pm$ 5	5	0.84	0.99
Barycz landfill, E	Landfill	19/03/2019	721		-53.9 $\pm$ 0.1	-294 $\pm$ 6	5	0.92	0.98
Królowej Jadwigi x 28 Lipca 1943	Unknown	19/03/2019	1067		-48.8 $\pm$ 0.1	-180 $\pm$ 3	4	0.79	1.00
Barycz landfill, W	Unknown	19/03/2019	1127		-50.2 $\pm$ 0.1	-210 $\pm$ 3	4	0.95	0.96
Mini landfill, Wodociągowa	Unknown	19/03/2019	1483		-51.0 $\pm$ 0.1	-207 $\pm$ 6	4	0.97	1.00
Senatorska, school	Unknown	20/03/2019	93		-58.2 $\pm$ 1.6	-250 $\pm$ 37	3	0.79	0.86
Pipeline, Balice -bis	Network gas	20/03/2019	269		-52.3 $\pm$ 0.5	-177 $\pm$ 11	3	0.86	0.68
Mazowiecka	Unknown	20/03/2019	313		-47.9 $\pm$ 0.4	-181 $\pm$ 7	3	0.76	0.97
Lewiatan, Kryspinów -bis	Unknown	20/03/2019	11251		-52.6 $\pm$ 0.0	-221 $\pm$ 1	3	0.99	1.00
AGH lab gas	Network gas	20/03/2019	950000000		-52.0 $\pm$ 2.0	-205 $\pm$ 0	2	1.00	1.00
AGH, sewage cover NE	Manhole	21/03/2019	1428		-51.3 $\pm$ 0.1	-338 $\pm$ 3	3	0.95	0.98
AGH, sewage cover SW -bis	Manhole	21/03/2019	2135		-40.4 $\pm$ 0.1	-162 $\pm$ 1	3	1.00	1.00
BP station, Warszawska	Network gas	21/03/2019	9275		-51.6 $\pm$ 0.1	-205 $\pm$ 1	3	0.97	0.90
AGH, sewage cover NW	Manhole	21/03/2019	17475		-33.3 $\pm$ 0.0	-146 $\pm$ 1	3	1.00	0.98
AGH, sewage cover N	Manhole	21/03/2019	17769		-36.1 $\pm$ 0.0	-190 $\pm$ 0	3	1.00	0.97
ArcelorMittal N	Unknown	21/03/2019	22141		-50.4 $\pm$ 0.0	-227 $\pm$ 1	3	0.96	1.00
AGH, white tank -bis	Unknown	21/03/2019	49164		-45.4 $\pm$ 0.0	-200 $\pm$ 0	3	0.99	0.98
Pniówek V, NE	Coal mine	22/03/2019	128		-50.4 $\pm$ 0.7	-180 $\pm$ 37	4	-0.20	0.94
Rekreacyjna, Czulówek	Unknown	22/03/2019	167		-47.9 $\pm$ 0.3	-272 $\pm$ 86	3	-0.10	0.97
Pniówek V, S	Coal mine	22/03/2019	537		-48.0 $\pm$ 0.2	-204 $\pm$ 12	4	-0.06	0.99
Borynia V & VI	Coal mine	22/03/2019	763		-51.4 $\pm$ 0.3	-214 $\pm$ 5	4	0.91	0.96
Debiensko II	Coal mine	22/03/2019	1107		-28.1 $\pm$ 0.1	-193 $\pm$ 4	5	0.89	0.98
Waszowice farm	Cow barn	22/03/2019	3232		-61.5 $\pm$ 0.0	-356 $\pm$ 2	4	0.93	1.00